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Vol. 29. No. 237. September 1943.

THE SOLVENT EXTRACTION OF LUBRICATING OILS.*

By H. ter Meulen.

The first solvent-extraction plant in the oil industry operated according to the Edeleanu process, and treated kerosine with liquid sulphur dioxide. In view of the great success obtained with this process, an extensive research in this field was started, and the theory of the extraction with solvents developed mainly in the direction of kerosine treating. When the industrial development of the lubricating oils proceeded so far that the natural supply of high-grade oils was insufficient to meet the demand, and solvent extraction showed itself to be able to produce high-grade oils from base materials which, until then, had supplied only second-grade lubricating oils, it was obvious that the process, together with the theory of the extraction process, was applied for lubricating-oil treating. The well-known triangle for the graphical interpretation of ternary systems was also used to explain the phenomena encountered in the lubricating-oil field. It was soon realized, however, that the extraction of lubricating-oils involved many more factors than the extraction of kerosine, and an endeavour was made to overcome these difficulties by various assumptions regarding the base composition of the lubricating oils.

The main difference between kerosine and lubricating-oil composition is the fact that the former consists of two or three groups of components, the paraffins, naphthenes, and aromatics, which in each group can be considered to react as a single compound. In the lubricating oils all the components can also be classified in these three groups, but the components of one group are so widely different in composition that they do not act similarly when treated with a solvent. This is due to the fact that there are so many combinations of paraffins with aromatics and naphthenes and *vice versa* that it is almost impossible to classify these combination molecules in a certain group.

This difference between kerosine and lubricating-oil extraction demonstrates itself immediately when we consider the methods by which these two processes are controlled. Kerosine-extraction processes are controlled by methods based on the chemical differences between raffinate and extract, such as percentage aromatics, determined by their reaction with sulphuric acid. Here we can speak of a definite extract with 100 per cent. of aromatics and a raffinate free of aromatics, which two products form the two corners of the famous triangle. Even if the raffinate can be separated and extracted by distillation in a large number of fractions, all these fractions behave similarly *versus* the burning qualities of the kerosine. Further, the boiling range of raffinate and extract are practically similar, which indicates that there has not been any extensive differentiation in the behaviour of the various fractions *versus* the used solvent.

* Received 10th May, 1943.

When we now consider the lubricating-oil extraction we see immediately the great difference in the two processes. There is not a satisfactory chemical method for the control of the separation. The refractive index method, based on the aromaticity of raffinate and extract, is not very illustrative of the quality of the raffinate, and can be used only for control of the process once the principles for a certain feedstock have been definitely established. The other methods in use, such as viscosity index and viscosity–gravity constant, are physical characteristics which have been shown to have a certain relation to the quality of the raffinate. However, here again these characteristics can be used only when we realize that they never have an absolute value. It is well known that the viscosity index is not an absolute value indicating whether an oil is satisfactory or not. Oils with high viscosity index (V.I.) are not always better than oils with a low V.I. when they are of different origin. It is not even a *sine qua non* that the higher the V.I. the better the oil. What is said of the V.I. also goes for the viscosity–gravity constant. But as the V.I. is in general use for the characterization of lubricating oils, it will be used further in this discussion.

From the above it will be clear that the study of the solvent extraction of lubricating oils is much more complicated than the study of kerosine extraction, and that the simple triangle representation is not sufficient to fully explain the phenomena encountered.

Before we can understand why one solvent has a different effect on a certain lubricating oil from another, it will be necessary to study the composition of the various lubricating-oil base stocks. It is my opinion that the investigation of the base stocks for solvent refining has mostly not been carried out completely enough to provide all data necessary for a full understanding of the results of the actual refining process.

Lubricating-oil fractions in crude oil are accumulated in the residue (or topped crude) from the normal distillation process. Besides these lubricating-oil fractions, the residues mostly contain other components, such as waxes and asphalt.

The separation of lubricating-oil fractions from asphalt is mainly performed by vacuum distillation, but it has been found that not all lubricating-oil fractions can be distilled off in high vacuum, as they decompose even below their reduced boiling point. Therefore the heaviest fractions can only be separated from asphalt by other processes, such as precipitation of the asphalt with propane. We may state here already that all single-solvent extraction processes fail to perform a sharp separation between raffinate and asphalt, and are applicable only on distillate lubricating oils. The combination of an asphalt-precipitating process and a solvent-extraction process will be discussed later.

Vacuum distillation does not produce a separation between lubricating-oil fractions and wax, as their boiling points are in the same range. The only way to perform a separation is by means of a dewaxing, with or without the application of a solvent.

The lubricating-oil fractions themselves consist of a large number of constituents, ranging from paraffinic hydrocarbons, via naphthenic, to aromatic hydrocarbons, with their combinations, and, in addition, each group consists of a large number of components with various boiling points. In view

of the application of the V.I. as the yardstick for the solvent-refining processes, we can classify the above groups according to their respective V.I.'s as follows :—

Paraffins high to very high V.I.
Naphthenes low to intermediate V.I.
Aromatics very low to low V.I.

The hydrocarbons containing two basic groups may show high or low V.I. As an example, di-cetylnaphthalene may be mentioned, which, notwithstanding its aromatic character, has a V.I. of 150.

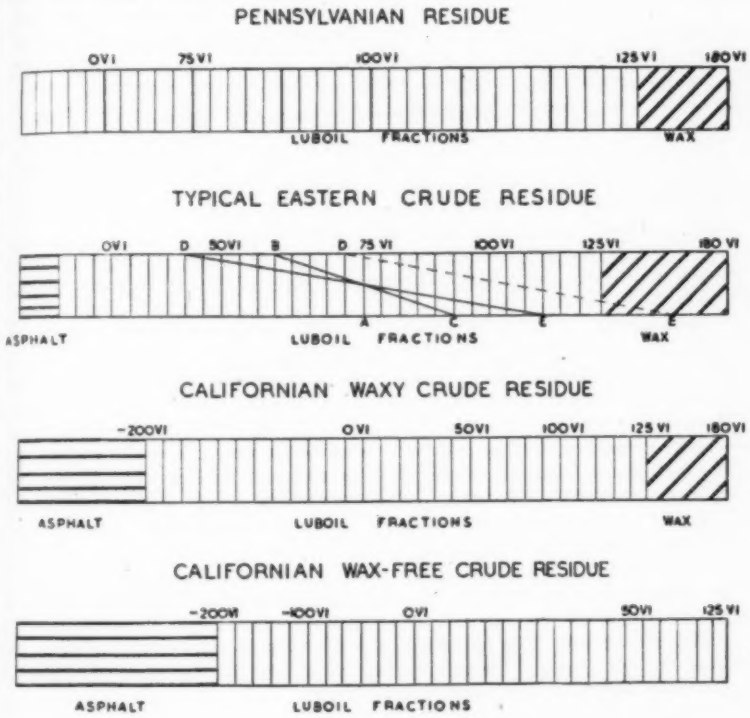


FIG. 1.

APPROXIMATE COMPOSITION OF VARIOUS CRUDE RESIDUES.

To visualize the main composition of various crude residues reference should be made to Fig. 1, which shows the composition of four representative residues of crude oils.

Along the abscissæ are plotted all the fractions of the residue, say forty fractions of 2·5 per cent., according to their V.I., starting with very low V.I. fractions at the left (the asphalts), and continuously increasing the V.I. until the highest V.I. fractions (the wax) are plotted at the right-hand side. These fractions are assumed to be obtained by successive

solvent extraction from the residue, extracting first the lowest V.I. fractions, and gradually increasing the extraction.

The ordinate indicates 100 per cent. of each fraction, and will be used to indicate later which percentage of a certain fraction will stay in the extract and which in the raffinate.

From this figure it can immediately be seen that the lubricating-oil content of the various residues is not the same, as is also the case with the distribution of the various lubricating-oil fractions according to V.I. The Pennsylvanian residue is asphalt free (or practically), and contains a relatively small percentage of low V.I. components. This total lubricating oil, when dewaxed, will therefore have a high V.I., and solvent extraction will give a high yield of very high V.I. lubricating oil. Quite opposite in composition is the Californian wax-free residue. Here, after removal of asphalt, a low V.I. lubricating oil remains, which contains a large proportion of intermediate V.I. fractions (naphthenic). Solvent extraction of this type of lubricating oil would yield a large quantity of raffinate with an intermediate V.I., say about 70 per cent. of 25–30 V.I. raffinate. Should an attempt be made to prepare high V.I. lubricating oil from this base stock, the yield would drop tremendously. A 90 V.I. raffinate can be obtained from this residue in a yield of 10 per cent.

An intermediate position is occupied by the typical Eastern residue, which contains a fairly high percentage of intermediate V.I. fractions, but also a good amount of high V.I. oils.

Incidentally, it may be pointed out that although the various base stocks contain varying amounts of constituents with certain V.I.'s, it does not necessarily follow that all the constituents of a given V.I. are identical. A 50 V.I. fraction in the typical Eastern crude is most probably, chemically speaking, different from a 50 V.I. fraction from the Californian wax-free residue. Consequently, it is to be expected that the extraction of constituents with the same V.I. from different base stocks will require different operating conditions, and sometimes even different solvents. This plays a very important part in the decision as to which solvents will have to be chosen in every case.

The representation of the composition of a base stock as given in Fig. 1 can also serve to explain the two main properties of a solvent, viz. solvent power and selectivity.

The comparison of these two properties of a solvent should always be done in comparable circumstances, such as temperature conditions, pressures, batch or continuous extraction, etc.

When a certain volume of solvent is mixed with a certain volume of oil, the fractions with low V.I. mix with the solvent, whereas the fractions with high V.I. form the raffinate phase. In the ideal case there should be a separation between two fractions, the one with the lower V.I. remaining in the solvent, the other with the higher V.I. in the raffinate. The point where this separation (point *A*, Fig. 1) is located depends on the "solvent power" of the solvent. The higher this solvent power, the more point *A* moves to the right, or the less solvent is needed to keep point *A* in its place.

It is, of course, well known that such an exact separation between two constituents never occurs, and that there will be a distribution of the various

adjoining constituents over the solvent and the raffinate phase, which distribution is governed by the extraction coefficient of each constituent in the solvent.

Therefore, the separation is not represented by a vertical line in point *A*, but by a sloping line, *e.g.*, that represented by *BC*, cutting line *A* at the 50 per cent. point. The steeper the line *BC*, the sharper has been the separation between the constituents in the extract and those in the raffinate. This sharpness of separation depends on the " selectivity " of the solvent under the given conditions. Line *BC* therefore represents the separation obtained with a solvent with higher selectivity than a solvent which would give line *DE* for separation.

Attention is directed to the fact that the yield of extract and raffinate in all cases mentioned (line *A* vertical, *BC* and *DE*) is the same, as the yields are represented by the surface of the areas to the left and right of the line of separation. However, it is obvious that the quality of extracts and that of raffinate are not the same. The raffinate obtained from solvent *BC* will have a higher V.I. and better qualities than the raffinate from solvent *DE*, as it contains less fractions with lower V.I. Further, it appears possible to obtain a raffinate with the same V.I. from both solvents when we move line *DE* to the right, deeper into the raffinate area, but the yield of raffinate will immediately decrease. This can be done by using more solvent, or increasing the solvent power of *DE* by increasing the temperature.

An actual example may give definite data. The base stock used was a Californian distillate (non-waxy), and extraction was carried out with aniline nitrobenzene. Results are given in the following table :—

TABLE I.

		Temp., ° F.	Yield raff.	V.I. raff.
a	100 per cent. Aniline 50 per cent. Nitrobenzene	75 35	88 78	35 35
b	200 per cent. Aniline 45 per cent. Nitrobenzene	75 35	85 85	39 33
c	100 per cent. Aniline 100 per cent. Nitrobenzene	75 35	88 66	35 47

A study of these results allows the following conclusions to be drawn :—

The selectivity of aniline is higher than that of nitrobenzene from cases *a* and *b*, where the yields of the raffinates with the same V.I. is higher for aniline, or at the same yields, the raffinate from aniline extraction has a higher V.I.

The solvent power of nitrobenzene is higher than that of aniline from case *c*, where the same quantity of solvent applied resulted in a much lower yield of raffinate for nitrobenzene.

Such results may serve as a guide for the selection of the best solvent, *e.g.*, when a raffinate with intermediate V.I. is required aniline would be chosen. But if we want to make the highest V.I. practically possible, say 60 V.I., nitrobenzene would be chosen because the application of aniline would require enormous quantities of solvent (low solvent power), which would prohibit its use.

From the solvents which are in practical application :—

Sulphur dioxide,
Phenol,
Furfural,
Chlorex,
Nitrobenzene,
Sulphur dioxide-benzene,

we can say that sulphur dioxide has the highest selectivity but a very low solvent power; whereas phenol and furfural have the lowest selectivity but a high solvent power. From this the conclusion may be drawn that for the extraction of Pennsylvanian or Eastern (midcontinent) lubricating-oil fractions, sulphur dioxide is in a very unfavourable position, as the solvent power for intermediate V.I. fractions is very low. The Shell Group have tried to improve the working effect of sulphur dioxide by adding benzene to it, thus increasing the solvent power but decreasing the selectivity, and bringing it in line with the other solvents. However, for the production of intermediate V.I. oils from naphthenic base stocks sulphur dioxide is the most suitable solvent.

As a matter of interest the following table gives a summary of an investigation on the extraction of Colon distillate with various solvents. The quality of the raffinate is characterized by the acid value and saponification number after oxidation with oxygen (312 hours at 120° C.).

TABLE II.

Solvent.	Yield raff.	Specific gravity.	n_D 20.	V.I.	Acid Value, 312 hrs.	Sap. Value, 312 hrs.
Phenol	70	0·883	1·4904	91	0·63	1·3
SO_2	70	0·880	1·4866	96	0·12	0·3
SO_2-benzene	70	0·880	1·4881	89	0·45	0·8
Cresol	70	0·884	1·4916	88	0·65	1·8
Chlorex	70	0·884	1·4896	90	0·60	1·4
Furfural	70	0·883	1·4900	88	0·40	1·0
Phenol	60	0·874	1·4856	96	0·38	0·9
SO_2	60	0·877	1·4841	98	0·10	0·2
SO_2-benzene	60	0·875	1·4862	92	0·12	0·3
Cresol	60	0·872	1·4848	96	0·12	0·4
Chlorex	60	0·876	1·4849	91	0·29	0·7
Furfural	60	0·875	1·4857	95	0·14	0·4
Phenol	50	0·867	1·4803	99	0·30	0·9
SO_2	50	—	—	—	—	—
SO_2-benzene	50	0·872	1·4853	94	0·10	0·3
Cresol	50	0·867	1·4814	99	0·10	0·3
Chlorex	50	0·870	1·4810	96	0·10	0·3
Furfural	50	0·870	1·4832	98	0·17	0·2

Here again the superiority of sulphur dioxide is coming to light, giving a good raffinate with a yield of 70 per cent., whereas the other solvents give yields between 50 and 60 per cent. for the same quality raffinate.

It is interesting to note that the specific gravity and refractive index are not the same for all the raffinates with the same quality. For sulphur

dioxide a raffinate with 0·880 specific gravity has the same oxidation stability as a furfural raffinate with a specific gravity of about 0·873. This matter will be returned to later.

It is rather difficult to give actual figures for a representation as shown in Fig. 1. But the Shell Group, in their research laboratories, have succeeded in separating a lubricating-oil base stock in ten fractions, which in this case were characterized by the refractive index. This base stock was then solvent extracted, and afterwards extract and raffinate again separated in ten fractions with the same refractive index as the ten fractions from the original base stock. Data were collected on Hendrick's base stock (naphthenic), and are given in the following table :—

TABLE III.

Fraction no.	Vol. %.	Ref. index n_D 20.	% each fraction in raff.	% each fraction in extract.
1	10·0	1·589	9·7	90·3
2	7·0	1·583	13·3	86·7
3	5·0	1·580	15·6	84·4
4	5·0	1·566	27·2	72·8
5	6·5	1·541	50·0	50·0
6	12·5	1·505	76·1	23·9
7	14·0	1·492	83·1	16·9
8	17·0	1·482	88·3	11·7
9	19·0	1·472	92·9	7·1
10	4·0	1·464	96·5	3·5
Raff. yield	—	—	65·0	—
Extr. yield	—	—	—	35·0

The data from the above table have been plotted graphically and are given in Fig. 2.

The top picture gives the relationship between the volume per cent. of each fraction on the crude oil and the refractive index, whereas the bottom picture shows the distribution of each fraction between extract (left side) and raffinate (right side). As could have been expected, the line of separation is not straight, but is a curve tapering to the ends. It is interesting to note that even the extreme fractions (very high or very low refractive index) are present in both phases, even if it is not in large amounts. For completeness sake it is mentioned that this particular extraction was carried out in seven stages, so a relatively sharp separation may already have been expected.

As a matter of interest, the distribution of the fractions was also determined when the extraction with furfural was carried out in four stages with three stages of backwash, at the same yield of raffinate (65 per cent.). The V.I. of the raffinate in the first case (without backwash) was 77, in the second case 84·3. The effect of the backwash system is obvious, the distribution line has turned a little clockwise, indicating the sharper separation resulting in a better raffinate. The figures also indicate that it is of advantage to reduce the number of stages of extraction and replace them by the same number of stages backwash.

Besides the solvent power and the selectivity of solvents, a third property —viz. the light-heavy selectivity—plays an important rôle. Until now

we have considered the base stock from the point of view of chemical constitution, but there is also a physical differentiation between the constituents—namely, their molecular size—which is represented by their boiling points. Every base stock contains constituents with lower and

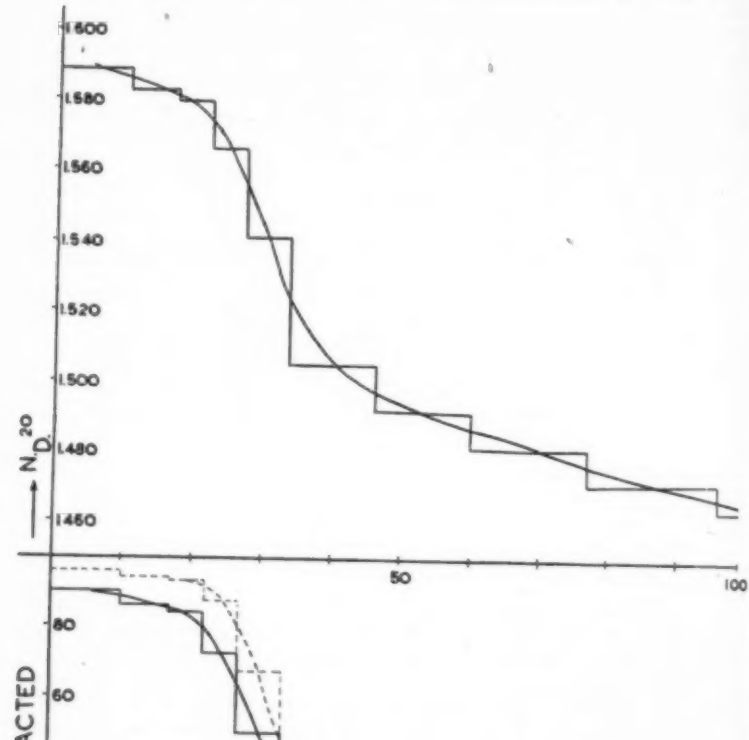


FIG. 2.

FRACTIONAL SEPARATION OF HENDRICKS BASE STOCK WITH FURFURAL.

higher boiling points, which from a chemical point of view belong in the same category of aromatics or paraffins. Some solvents have a pronounced solvency for lighter hydrocarbons *versus* the heavier hydrocarbons, which means that a larger fraction of a light paraffin will be dissolved in

the extract than of the similar (according to V.I.) heavy paraffin. An attempt has been made to express this property of a solvent in Fig. 3, which expresses the three properties of solvents in one picture.

The front plane of the space figure represents the fractions of the base stock, separated into the various V.I. constituents, similar to Fig. 1. The co-ordinate in depth represents the boiling range of every V.I. group of constituents from high to low boiling points. The separation by a solvent is shown by line CC' in the front plane, and if there was no light-heavy selectivity, the total separation would be given by plane $CC'DD'$. However, when light-heavy selectivity plays a rôle, this means that more of the

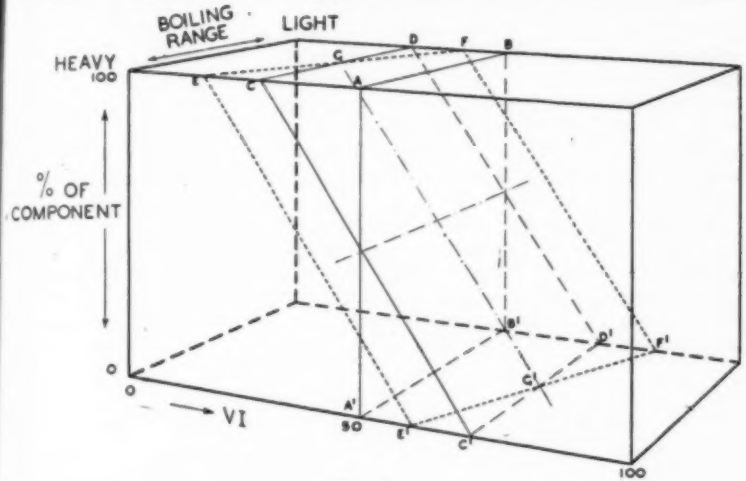


FIG. 3.

STEREOMETRIC VIEW OF SOLVENCY, SELECTIVITY, AND LIGHT/HEAVY SELECTIVITY.

light paraffinic constituents are dissolved in the solvent than of the heavy paraffinic constituents, therefore line CC' will move to the left (EE'), whereas line DD' will move to the right (FF'), and the plane $EE'FF'$ will represent the total separation. Summarizing, we can say that the extract from a solvent which gives plane $CC'DD'$ will contain less lighter high V.I. fractions than the extract produced by a solvent which gives plane $EE'FF'$, which discrepancy is indicated by the content of $GG'FF'DD'$. Fractionation of the second extract should give a light distillate with a higher V.I. than the heavier fractions or the residue. The following actual figures illustrate this :—

TABLE IV.

	Vol. %.	V.I.
Total extract . . .	100	64
Distillate I . . .	26·0	91
„ II . . .	27·4	60
„ III . . .	26·0	47
Bottoms	20·0	40

Actually, therefore, the fraction I should have been in the raffinate instead of in the extract. It can be said that the light fractions have been over-extracted, the heavy fractions not sufficiently extracted.

The remedy for such a case is obvious—viz., the cuts should have been made before the extraction and extracted separately, by which procedure the extraction can be adjusted to such an extent for each cut that similar quality products would have been obtained for each cut. This method is called the split-feed extraction, and is always advisable if the solvent used possesses a high light-heavy selectivity, and the base stock a wide variety of fractions from light to heavy.

Such solvents are sulphur dioxide and furfural. It is obvious that this phenomenon appears most pronounced when the feed stock is a very wide cut, and it is also dependent on the type of base stock. Naphthenic base stocks which are extracted to a moderate extent with sulphur dioxide are not subjected to this phenomenon, but it begins to come into the picture when the extraction is carried further, because, as said before, the solvent power of sulphur dioxide for intermediate V.I. constituents is very poor, and the molecular size of the constituents then becomes of more and more influence.

Further, the peculiar effect this light/heavy selectivity may have on the viscosity of raffinate and extract should be mentioned. As is known, the viscosity of the raffinate is generally lower than that of the extract, because the aromatics have higher viscosities than the paraffins. However, it is possible that the raffinate is more viscous than the extract, which is shown in the following tabulation :—

TABLE V.

Solvent.	Original viscosity.	Yield. 80%.	70%.	60%.	50%.
Oil V.I., 100	161	—	—	—	—
Phenol	—	163	169	174	187
SO_2 benzene	—	163	166	170	170
Chlorex	—	154	160	168	175
Cresol	—	142	150	162	173
Furfural	—	154	155	156	183
Oil V.I., 80	150	—	—	—	—
Phenol	—	122	112	107	110
SO_2 benzene	—	130	133	140	150
Cresol	—	125	114	110	125
Furfural	—	133	128	127	127

Here it is shown that by further extraction of the oil with a V.I. of 100, the viscosity of the raffinate increases. This is due to the fact that, as there are practically no more aromatics to remove, the solvent is dissolving the paraffinic fractions, and mostly the lightest, first resulting in an increase in the viscosity.

For the extraction of the 80 V.I. base stock the viscosity decreases first, and after all the aromatics are removed the paraffins begin to dissolve. When the solvent has a pronounced light/heavy selectivity a considerable amount of the light paraffinic fractions are already removed during the

extraction of the aromatics, and therefore the overall slope of the line will be flat, without a deep minimum, such as is shown by furfural (Fig. 4).

A solvent with a small light/heavy selectivity has not yet removed the lighter paraffinic constituents with the aromatics, and therefore the viscosity of the raffinate drops deeper and then increases again, because a difference in solubility of light and heavy fractions always exists, and this effect then fully comes to light by an increase of the viscosity.

Before it was stated that the raffinate obtained with SO_2 had the highest specific gravity and refractive index (see Table II). This also is caused by the high light/heavy selectivity, because the lighter constituents were readily removed with the aromatics in the first extractions.

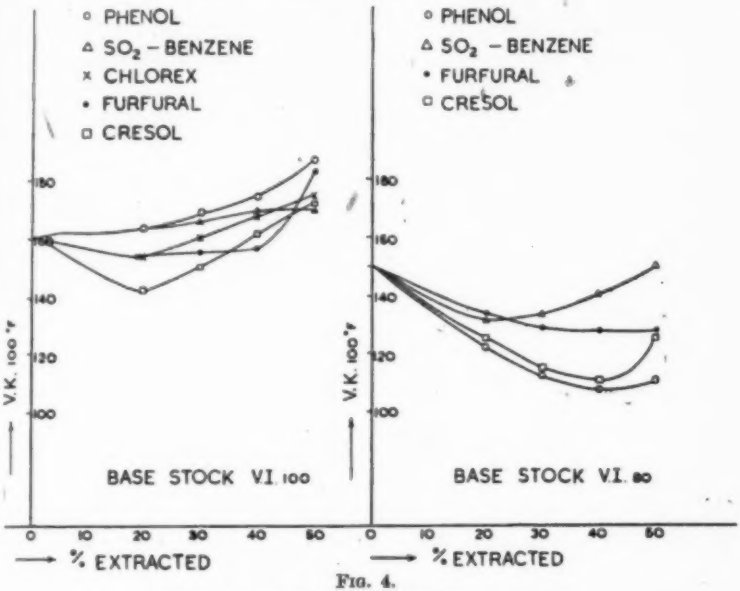


FIG. 4.

KINEMATIC VISCOSITY (CENTISTOKES) AT 100° F.

This characteristic property of all solvents is the reason for the impossibility of extracting S.R. residues immediately with a single solvent to a suitable raffinate. The residues represent the ultimate case of a very wide cut, as the heaviest components, such as asphalt and resins, are present. A single-solvent does not have such a low light/heavy selectivity that all asphalt is removed from the raffinate into the extract layer. Therefore single-solvent extraction processes are applicable only to distillate fractions. The only process capable of processing a S.R. residue is the Duo-Sol process, using a mixture of phenol-cresols as the aromatic solvent and propane as the paraffinic solvent. These two solvents are only slightly miscible, and produce two layers. The solubility of asphaltenes in propane is practically negligible, and therefore all the

asphaltenes are precipitated from the raffinate layer into the extract layer. The conclusion may be drawn that it would also be possible to remove the asphaltenes from a S.R. residue by propane precipitation and then solvent extracting the remaining asphalt-free lubricating oil with a single solvent. This was carefully investigated, but it appeared that besides the asphaltenes other very heavy components were present (resins) which could not be extracted. These resins were not precipitated sufficiently by propane alone, but the combination propane-phenol removed all the heavy components into the extract (phenol layer).

From this it is obvious that the Duo-Sol process maintains an exceptional position in the solvent-extraction field, and it is very doubtful whether a single solvent will be found which would produce the same results.

THE INSTITUTE OF PETROLEUM

A MEETING of the Institute of Petroleum was held at the Royal Society of Arts, W.C. 2, on Thursday, 24th June, 1943. DR. DUNSTAN occupied the Chair.

The following paper was read :—

"The Solvent Extraction of Lubricating Oils," by Dr. H. ter Meulen. (See pages 237–248.)

DISCUSSION.

THE CHAIRMAN said he thought they were all agreed that the author had given an exceedingly interesting analysis of a highly complicated problem. He was particularly concerned in his remarks on the upgrading of an apparently useless substance derived from a primary material which was thought originally to be valuable *sui generis*; in other words, the extracts themselves might turn out to be of considerable value in industry.

MR. E. S. SQUIRE asked whether Dr. ter Meulen could say whether a temperature gradient was used in the seven-stage extraction plant? Further, what was the effect of temperature on the light/heavy selectivity?

DR. TER MEULEN replied that this seven-stage extraction was carried out at a temperature gradient, because this was necessary to get a decent separation with furfural. Otherwise they probably would not have had even this sharp fractionation. The effect of the temperature gradient was that the starting-point "A" was moved to the right for every step. They intended to move it to the right, because nature would move it to the left if it was left at the same temperature.

The solubility of the higher V.I. fractions got less and less. If a temperature gradient were not taken, this solubility would decrease for every stage. Operating on a temperature gradient it was moved back to the same point, to the right, resulting in the same concentration of extract in every stage.

MR. E. J. DUNSTAN said that he had had an auctioneer's conversation with the Chairman a moment or two ago in which he declined to participate in the discussion. That was largely due to the rather severe shock which he had had from the implications of the author's lecture. Being a refinery man, he could see the complications in his life increasing very rapidly.

First of all, he thought the author should be heartily congratulated on some work which was of really primary importance in lubricating-oil refining. There had already been recognition of the fact that a very sharp separation was not obtained, but the encouragement to continue with that separation had not really been forthcoming, due to lack of basic information. This paper certainly contained quite a considerable amount of the information required.

He thought that the first stage was recognition of the fact that lubricating-oil distillates should be handled separately—he thought that was implied in the paper—in order to achieve by methods not already available that light/heavy selectivity. Yet he felt from an examination of the literature which had been written on the subject that there was still a great tendency to solvent extract long cuts That might have been altered and he might not be up to date on it, but certainly in the earlier days the tendency had been to extract long cuts and subsequently to fractionate after the contact treatment.

The first stage appeared to be selective distillation—very careful distillation—and the application of the solvent afterwards. The next stage to that was the introduction of numerous stages in the solvent-extraction system. He thought that there they

were getting into a mechanical problem—one which would have to be solved by some means or other.

Working an SO_2 process, he looked upon that problem as a very serious one. SO_2 was a solvent that presented the difficulty of maintaining under prolonged conditions gas-tight equipment, and numerous stages, involving a large increase in equipment which had to be mechanically maintained. Nevertheless, it was the mechanical end which appeared to him to be the one to tackle next if this very desirable picture was to be realized to any degree at all.

DR. TER MEULEN said that he was sorry if in going through this pre-print he had omitted a statement about this correction of the light/heavy selectivity. Of course, the solving of this had to be done by separating the feed-stock in the various fractions. The remedy for such a case was obvious. The cut should have been made before the extract and extracted separately, by which procedure the extraction could be adjusted to such an extent for each cut that similar quality products would have been obtained for each cut. That was, as had been said, what should have been done, and in quite a good many plants it was already done.

Mr. Dunstan had touched on a point of the mechanical adventure, as he might call it, into which they were going when they made further separations, because every product would require a solvent recovery. The trouble which was visualized would complicate the plant enormously—he agreed with that. However, there was a Union Oil plant in California which was working on that principle and making three products already. They had gone into that very carefully. The first plant was working SO_2, and the other with SO_2-benzene. In the first they extracted so far that they got a raffinate with only about 50–60 V.I. In the second plant (because the solvent power of SO_2 was too low to obtain a good raffinate with reasonable quantities of solvent) they extracted with SO_2-benezene and made a raffinate with about 90 V.I. The extract which was obtained in that plant was one of those intermediate cuts. Incidentally, in that case it was second-grade lubricating oil, so it was not actually a waste product.

Although they were going in for more complicated plants (with higher maintenance costs and all the other things, on which he agreed with Mr. Dunstan completely), they would give, in his opinion, very high returns, which was of course the purpose for which they were working. It had all only to do with whether it paid or not. He thought that when these intermediate fractions were developed they would find that the value of the fractions would not be considered to be of an intermediate, but in certain cases of even higher value.

MR. E. J. DUNSTAN thanked Dr. ter Meulen, but added that he had only served to emphasize his fears.

THE CHAIRMAN said that one point struck him in passing. Perhaps the author could help them. How were these solvents selected? What had been the basic reason, for example, in selecting chlorex?

As a chemist, one imagined that a selective solvent entered into some sort of loose chemical combination. When the aromatics were dissolved out by SO_2, for example, there was something in the nature of a union between those two. He wondered whether the author could give some idea of what he called the basic principles. Was it just sheer empericism; or was chlorex developed by scientific reasoning?

DR. TER MEULEN replied that there had been a lot of speculation on that, much of which afterwards proved to be not complete hits, but also not complete misses.

The Amsterdam laboratory of the Bataafsche Petroleum My. had done a tremendous amount of work in selecting various solvents based on certain reasoning. They found, working on the polarity of a solvent, that they could reasonably predict whether or not that solvent would be suitable. There were, of course, many misses in that too; there were still cases which did not follow the rule.

Certain polar solvents showed better solvency for—he did not want to use the term aromatic fractions—low-viscosity index fractions then other non-polar solvents. *iso*Propyl alcohol, for example, did not show much polarity one way or the other. They had done some work on that, and had found that *iso*propyl alcohol was completely unsuitable. All these things could be separated into certain polarity groups

which might indicate whether they were suitable or not. He agreed with Dr. Dunstan that a definite basis why a certain compound acted as a solvent and why another did not was not definitely stated. He did not think that that had been definitely fixed for all matters of solvents.

MR. JARMAN said he did not know whether it was within the scope of the discussion, but, in view of the remarks which had been made about the extracts, he wondered whether the author was able to give any indication of what should be considered desirable properties of the extracts as distinct from the raffinates in these separations.

DR. TER MEULEN replied that Mr. Jarman was touching on a point which did not exactly come within the scope of the paper. He only wanted to deal with the surface of this whole field, whereas Mr. Jarman would like to pin him down to certain statements about what was actually wanted.

He could give one example which might explain the whole thing. If an extract from a certain Californian oil were taken and distilled in very high-boiling fractions, from an artistic point of view, very nice products were obtained. They were highly coloured, highly fluorescent, and they were absolutely solid, but if a block were made of them, the next day it would be found that it had spread out. If the material were hit with a hammer it just split into a thousand pieces. If it were desired to obtain that product from other products there would be complete failure, because it was not in it. That was only one example. The purpose for which the extract was wanted, and the extract available would not always fit together.

It was only possible for him now to point out what scope there was in that field. Everybody who was interested in it had a field which was so wide that he might find something which suited his special purpose; or maybe he would not find it—he did not know.

THE CHAIRMAN suggested that in other words it depended on the crude one was working with.

DR. TER MEULEN said that was so, and that even with the same V.I. the fractions were not the same.

THE CHAIRMAN said that one of these days they would hope to have a very full discussion on the utilization of these remarkable materials.

MR. PAYSANT said that, being interested in running a solvent plant, he could sympathize with some of the points that had been made. He had asked himself at times —as this meeting might ask itself—Why did they extract? Why was this process necessary? He thought the answer was that no other process commonly used could do the same work. They could distil oils and do one kind of classification; they could extract them and do another kind of classification.

If they were just out for two products, they had a number of choices amongst the processes, but it looked as though the tendency would be to make a number of products —not just the two end ones, but a number of the intermediates. It had been done; he thought mention had been made of breaking up the oil into narrow fractions by distillation first and then extracting. He believed that the opposite had been done as well, but these procedures were laborious, and he wondered whether the present problems did not alter the choice which Dr. ter Meulen had made in choosing the two-solvent processes rather than the single solvent.

He would like to know more about another point, since it did not seem quite obvious that light/heavy selectivity was altogether a disadvantage. It seemed to him that it might be put to some advantage if at later stages they wanted to cut into oils at very specific points, as they did now with distillation.

Perhaps he could illustrate that in another way. Extraction was used because the job could not be done by distillation; yet in examining an extract Dr. ter Meulen had distilled it, and he had distilled it to examine that light/heavy selectivity. It seemed to him that that was a weapon which might be useful for making these special products at a later stage. In other words, a solvent with marked light/heavy selectivity might be preferable to this two-solvent process, which in effect corresponded to a uniform selectivity.

DR. TER MEULEN replied that the point raised was indeed an interesting one, because it might give the separation of very small quantities of part of the intermediates wanted. He used the data from the table to show that the extract contained high V.I. fractions, but it should not be forgotten that these fractions which were taken out formed not the full group of products in the depth of the space configuration, but only part of that slice it was desired to cut out. What they were aiming to do was to cut out one, two, or three slices from this space configuration. If that were done with a light/heavy selective solvent and it was afterwards distilled, only the back part was cut out from that slice—assuming that the light was at the back—and not the front part, because the front part was not in the extract, it was in the raffinate. Only the back part was in the extract and could be distilled out.

For example, a certain product combination of a paraffin aromatic could be taken, such as ethyl benzene, or any high product like that. There were there hydrocarbons in the same group: ethyl benzene, butyl benzene, propyl benzene. They were in the depth of the picture. Ethyl benzene could be taken at the end and, say, butyl benzene at the beginning. The ethyl benzene was in the extract because it was the lightest, but in the raffinate was the butyl benzene, and the propyl benzene was divided between the two. So only part of that special group was recovered. The results were that the maximum of a special group was not obtained.

MR. PAYSANT said that he thought his question was really answered, but he would like to think about it to be convinced. Was it certain that another method would get the whole, in this case, of the propyl benzene in one group?

DR. TER MEULEN said that it was certain the Duo-Sol process made a steeper cut through the whole thing because it had no light/heavy selectivity. It only depended on how far one extracted with the Duo-Sol plant. It was possible to go straight to the end by adding a lot of solvents and operating at higher temperatures; they could cut deeper into the higher V.I. business, and all the things were in the extract. Then they could theoretically decrease the solvent amount, which would leave another cut in the extract, more to the left, giving a second raffinate which was actually the cut wanted. So anything could be adjusted, decreasing gradually the solvent amount.

THE CHAIRMAN brought the meeting to a close by saying that it was his very pleasant duty to ask for the heartiest possible vote of thanks to Dr. ter Meulen, who had dealt with a most intricate subject in an extraordinarily clear and lucid fashion.

The vote of thanks was carried with loud applause.

A MODIFICATION OF THE C.F.R. BOUNCING PIN SPRING-TENSION BALANCE AND INSTRUCTIONS FOR USE.

By P. Draper.*

Introduction.

The spring-tension balance designed in the Shell Laboratories and described in the *J. Inst. Petrol.*, Vol. 28, p. 209, had proved so successful, particularly in enabling repeatable octane ratings to be obtained in the range of 90–120 O.N., that the Institute of Petroleum requested the C.F.R. Committee in America to co-operate by designing a less costly apparatus. This has been done very successfully by the Ethyl Gasoline Corporation Yonkers' Laboratory, and the instrument, which is described in this report, has certain advantages over the original model.

Description.

The balance is illustrated in Fig. 1, which is self-explanatory, while further working drawings are given in Figs. 2 and 3.

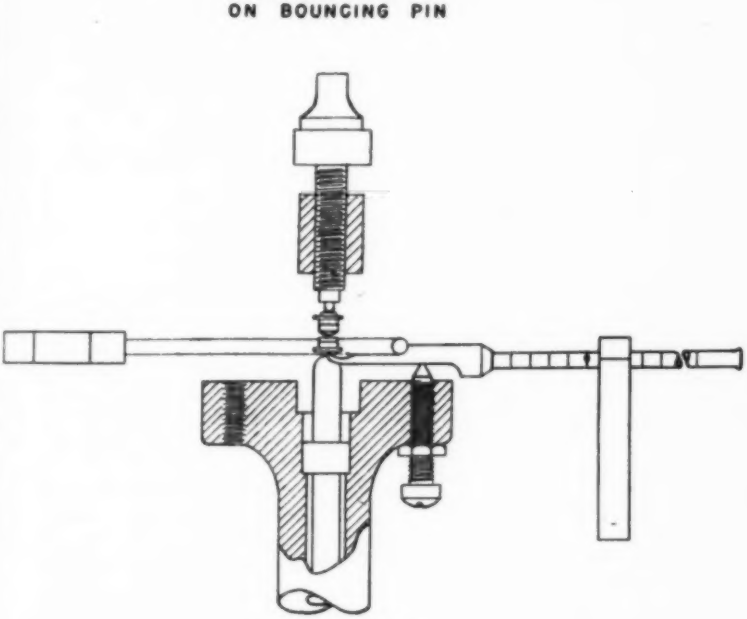
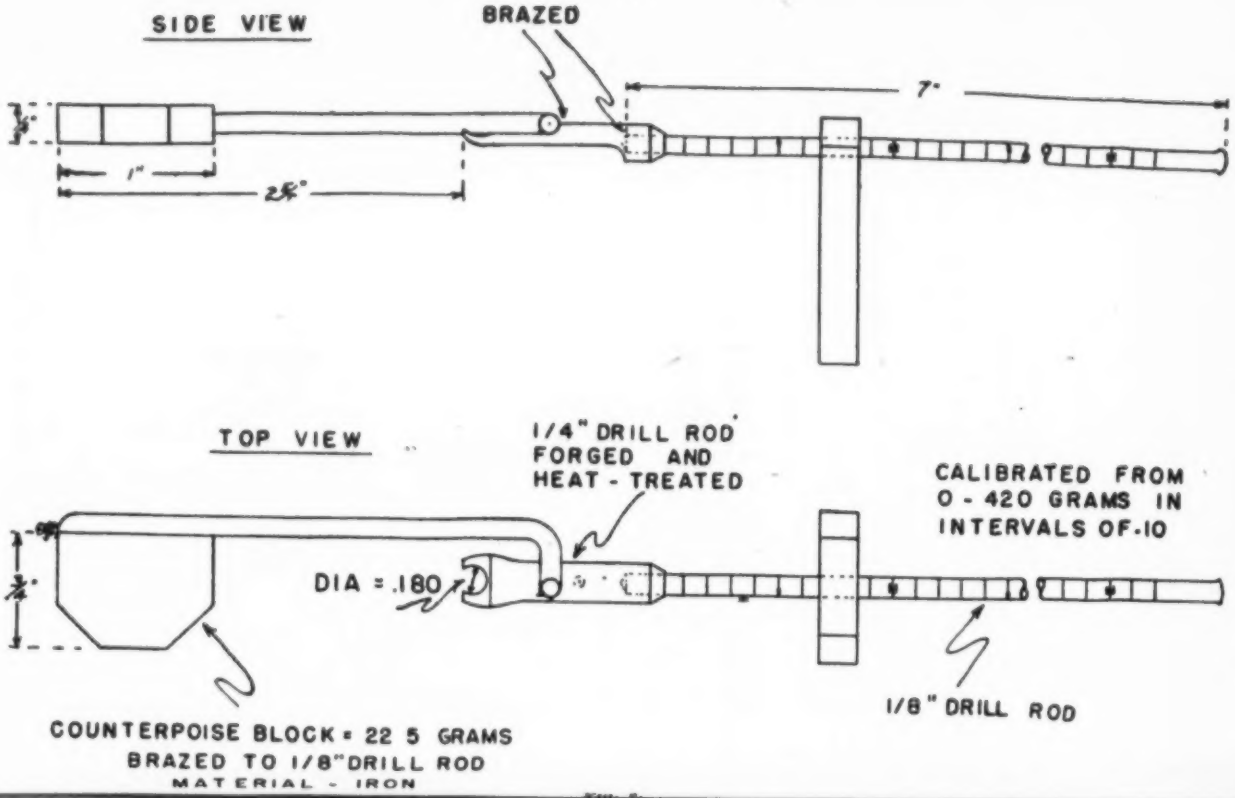


Fig. 1.

* The Asiatic Petroleum Co., Ltd.


SIDE VIEW
BRAZED
7"
1"
2⅝"
TOP VIEW
1/4" DRILL ROD
FORGED AND
HEAT - TREATED
CALIBRATED FROM
0 - 420 GRAMS IN
INTERVALS OF 10
DIA = .180
1/8" DRILL ROD
COUNTERPOISE BLOCK = 22 5 GRAMS
BRAZED TO 1/8" DRILL ROD
MATERIAL - IRON

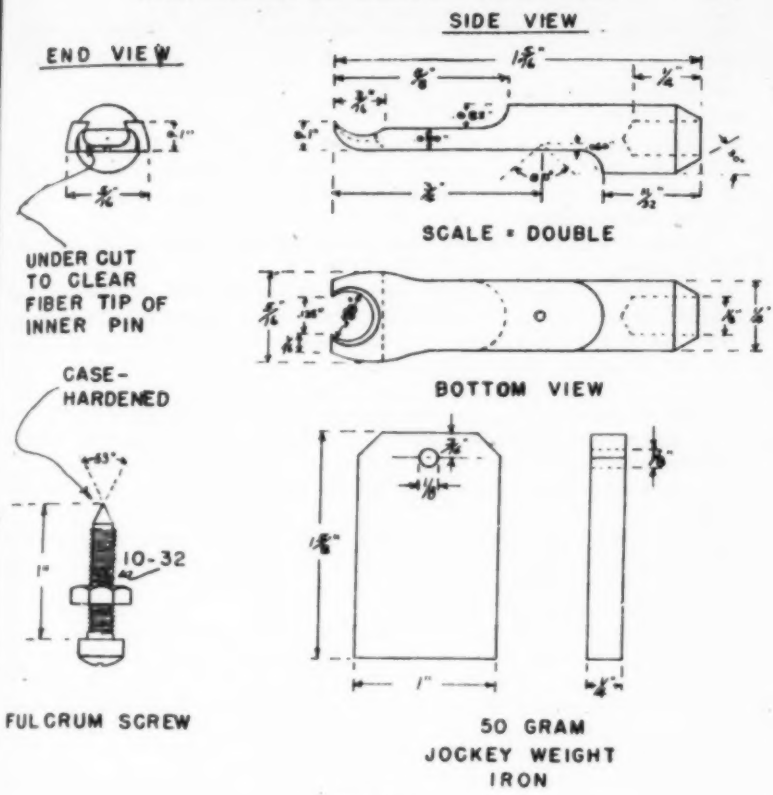


FIG. 3.

The fulcrum screw is inserted in the tapped hole in the bouncing-pin head which is nearest the operator when the lower leaf-spring is on the left-hand side. It is suggested that each bouncing pin in use should be permanently fitted with such a case-hardened screw.

(*Note.*—Some bouncing pins are not drilled and tapped in this position. These require an S.A.E. No. 10 0·19-inch-dia. 32 T.P.I. tapped hole through the head on a line 90° to the bridge piece $\frac{3}{4}$ inch from the centre of the pin.)

When the fulcrum screw is locked at the correct height it takes a matter of seconds only to mount the balance beam and to commence setting the spring tensions.

The chief advantages are that the beam has 3-point suspension reducing out of alignment friction, and it does not have to lift the pin itself, also reducing friction.

A disadvantage is that the tension of the plunger spring cannot be measured with the balance, but this is not of great importance, as

this tension can be set sufficiently accurately by the means described later.

Method of Use.

This is very similar to the method employed with the Shell instrument, but is detailed below, in order to save confusion. The method of arriving at the tensions required is not described again; reference should be made to the previous paper.

Assuming that the bouncing pin has been carefully cleaned and assembled, the following procedure should be adopted.

1. *Plunger Tension.*—Remove the plunger assembly from the unit and adjust the tension screw so that the plunger just commences to move at 455 gms. (1 lb.) and 570 gms. (1¼ lb.) respectively, and mark the positions of the adjusting screw with a pencil for future reference. Leave the tension set at 530 gms. and replace in bouncing pin unit.

This setting may be accomplished with the aid of a platform balance.

2. *Lower Leaf-spring Tension.*—See that the leaf-spring contacts are correctly aligned and set with a gap of approximately 0·001 inch.

Mount the balance and set the fulcrum screw so that the beam is horizontal.

Adjust the lower leaf-spring screw until the lower contact commences to vibrate at settings of 180 gms. and 245 gms., marking the adjusting screw for future reference.

Leave this spring set at 180 gms.

(The tension is read from the inner face of the jockey weight.)

3. *Nett Balancing Force of Upper Leaf Spring and Plunger Spring.*—Adjust the upper leaf-spring screw until both leaf-springs and the plunger commence to lift at settings of 270 gms. and 330 gms. respectively. Mark the screw for future reference.

This setting should be left at 310 gms.

4. *Final Setting.*—Remove the spring-tension balance and set the contact gap to 0·003 inch (its limits being 0·003–0·005 inch).

The bouncing pin is then set for operation, and a minimum of alteration should be made within the limiting marks made on the adjusting screws. No alteration is permissible outside these limits.

Setting for Testing Low Octane Fuels (up to 80 O.N.).

The engine is warmed up and operated at standard knock intensity by running on a fuel of known Octane Number (between 65 and 80) at the appropriate compression ratio or micrometer setting indicated by the A.S.T.M. Guide Tables. A knockmeter reading of 55–60 should then be obtained by *very slight* adjustment of the contact gap within the limits specified above. Should it be necessary to carry out any other adjustment within the marked limits it should be remembered that the nett balancing force of the upper leaf-spring and the plunger determines the sensitivity of the knockmeter, while the tension of the lower leaf-spring should be sufficient to prevent the recording of "combusion pressures" as distinct from knocking.

Setting for Testing High Octane Fuels (above 80 O.N.).

When testing fuels above about 80 O.N. a check test should be applied to ensure that "combustion pressures" are not being recorded on the knockmeter. This check consists of operating the engine on a non-knocking fuel (toluene or high octane number reference fuel blend) at the compression ratio at which testing is to be carried out, if a knockmeter reading of more than five divisions is recorded the combustion pressure effects may be eliminated by increasing the downward tension of the lower leaf-spring up to a maximum of 245 gms. This setting will usually be required for testing 100 O.N. fuels. For testing fuels over 100 O.N. it may be necessary to increase the tension to 300 gms. (see *J. Inst. Petrol.*, Vol. 27, p. 191).

Notes.

At the present time it does not appear that the C.F.R. Committee intend to adopt this apparatus as standard equipment although they have opened negotiations with an Instrument Manufacturer concerning possible supply. The reason for this is probably that in America high-O.N. aviation fuels are at present rated by the Aviation 1 C. Method, which does not employ a bouncing pin.